

# **Report for 2003ID11B: Validating Meta(loid) Flux Predictions from Lake Coeur d'Alene Sediments Using Contaminated Ponds as Mesocosms**

- Conference Proceedings:
  - Finkelnburg, Douglas C., Gordon R. Toevs, and Matthew J. Morra. 2005. Metal(loid) Solubility in Persistently Reducing Mining-Impacted Wetland Sediments, In Abstracts of the 86th annual meeting of the AAAS Pacific Division Western Society of Soil Science/AAAS, Ashland, OR, pg. 55.
  - Finkelnburg, Douglas C., Matthew J. Morra, Gordon R. Toevs, and Vladimir Borek. 2005. Alkalinity Measurement in Mine-impacted Wetland Sediments Using Gas Chromatography, In Abstracts of the 15th Annual V.M. Goldschmidt Conference, Moscow, ID, abstracts online at [http://www.the-conference.com/2005/gold2005/web\\_pdfs/G07.pdf](http://www.the-conference.com/2005/gold2005/web_pdfs/G07.pdf), pg. A814.
  - Toevs, G., Polizzotto, M., Morra, M., Strawn, D., Fendorf, S., Bostick, B. 2005. Arsenic Mobilization in Mine-Impacted Sediments, In Abstracts of the 15th Annual V.M. Goldschmidt Conference, Moscow, ID, abstracts online at [http://www.the-conference.com/2005/gold2005/web\\_pdfs/G07.pdf](http://www.the-conference.com/2005/gold2005/web_pdfs/G07.pdf), pg. A617.
  - Toevs, G., M. Polizzotto, M. Morra, D. Strawn, S. Fendorf, and B. Bostick. 2004. Arsenic Mobilization as a Function of Redox Changes in Mining-impacted Sediments. In ASA Abstracts, Seattle, WA, 2004 American Society of Agronomy Abstracts on CD.

Report Follows

**Title:** Validating Metal(loid) Flux Predictions from Lake Coeur d'Alene Sediments Using Contaminated Ponds as Mesocosms

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**Primary PI:** Matthew J. Morra

**Other PIs:** Daniel G. Strawn

Project Class:

**Student Support:**

Two students are currently working on the project. Gordon Toevs is a Ph.D. student funded by the Inland Northwest Research Alliance and Douglas Finkelnburg is funded by a University Presidential Scholarship. Although stipends for both students are provided by other sources, IWWRI funding has been essential to support operating and travel expenses for these students.

**Publications:**

Finkelnburg, Douglas C., Gordon R. Toevs, and Matthew J. Morra. 2005. Metal(loid) Solubility in Persistently Reducing Mining-Impacted Wetland Sediments, In Abstracts of the 86th annual meeting of the AAAS Pacific Division Western Society of Soil Science/AAAS, Ashland, OR, pg. 55

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Toeve, G., M. Polizzotto, M. Morra, D. Strawn, S. Fendorf, and B. Bostick. 2004. Arsenic Mobilization as a Function of Redox Changes in Mining-impacted Sediments. In ASA Abstracts, Seattle, WA, 2004 American Society of Agronomy Abstracts on CD.

### **Project Overview:**

Lake Coeur d'Alene (CDA) in Idaho is the second largest natural lake in the Inland Northwest. Over the last century Lake CDA has become a major collecting bed for As, Pb, Cd, Zn, and other contaminants. The USGS has estimated that as much as 85% of the lake bottom is contaminated with metal(oids). Despite this contamination, lake water quality typically meets regulatory guidelines. Unfortunately, the median concentrations of As, Pb, and Zn in the porewater from the lake sediments are considered chronically or acutely toxic. The overriding concern is potential release of the accumulated metal(oids) into the overlying water column. However inadequate information exists to make accurate metal(loid) flux predictions in changing redox environments. Our objective was to characterize key geochemical properties that control metal(loid) flux from sediments to the overlying water column in order to predict the impact of redox changes in altering this flux. To accomplish this goal we characterized the lake sediments and made use of a novel approach using contaminated ponds along the CDA River as mesocosms. These ponds have been contaminated by the same events that have transported contaminants to Lake CDA and thus allow us to determine how redox changes impact flux of metal(oids) to the overlying water column.

Total metals in lake and pond sediments were determined by analyses of HF-Aqua regia digest solutions using ICP-AES. Porewater trace metal concentrations were determined from ICP-MS analyses of acidified samples collected in equilibrium dialyzers inserted into the sediments and retrieved after a 4-week equilibrium period. Anion concentrations were determined using non-acidified porewater samples analyzed using ion chromatography. X-ray absorption near edge structure (XANES) spectroscopy was used to determine sulfur oxidation states and speciation. Solid phase Fe was speciated from linear combination fitting of the deconvoluted curves obtained from extended x-ray absorption fine structure (EXAFS) spectroscopy.

Maximum lake-sediment concentrations of As, Pb, Cd, and Zn were 278, 5 169, 37, and 3 686 mg kg<sup>-1</sup>, respectively. Lake sediment contained from 3.9 to 10.5% Fe. Maximum As, Pb, Cd, and Zn lake-porewater concentrations were 1.21, 0.142, 0.004 and 0.530 mg L<sup>-1</sup>, respectively. Fe in the lake-porewater increased with depth throughout the profile to a maximum of 53 mg L<sup>-1</sup>, whereas As and Mn increased below the suboxic boundary and remained elevated throughout. The lake was oxic in the overlying water column, suboxic in the top 3 cm of sediments, and anoxic at depths below 5 cm. XANES analysis of the solid phase indicated pyrite increased with depth to comprise about 50% of the total S in the 30- to 36-cm sample. However, the Fe to S ratio indicates S does not dominate metal(loid) sequestration. EXAFS indicated siderite dominated the solid iron phase and exceeded 70% of the iron species in the 30- to 36-cm sample. Oxyhydroxides were present in the lake at the sediment-water interface.

Maximum pond-sediment concentrations of As, Pb, Cd, and Zn were 298, 14 598, 55, and 10 812 mg kg<sup>-1</sup>, respectively. Pond sediment contained 7.2% to 10.1% Fe. Although the sediment contamination in the ponds significantly exceeds the lake-sediment levels, As, Pb, and Cd in the porewater was near detection limits and the maximum Zn was 0.472 mg L<sup>-1</sup>. Iron in the pond-porewater increased throughout the profile to a maximum of 179 mg L<sup>-1</sup>, Mn increased at the suboxic boundary and remained elevated throughout the profile. Porewater As was near or below detection limits, 0.040 mg L<sup>-1</sup>. The pond was determined to be suboxic in the overlying water column and at the sediment water interface and anoxic throughout the sediment profile.

The striking difference between the Fe and As porewater concentrations in the lake and pond suggest different mechanisms of metal(loid) release, flux, precipitation and dissolution. In the lake, as the mine tailings (reduced primary minerals) accumulate at the oxic sediment-water interface they begin to oxidize, dissolution occurs, and oxyhydroxides precipitate. These oxyhydroxides act as scavengers for the metal(loids) as they diffuse toward the overlying water. This series of reactions prevents metal(loids) from entering the water column. However, as additional sediment is deposited, the oxyhydroxides and coprecipitated metal(loids) are buried and become unstable as the redox environment becomes anoxic. This accounts for the increase of Mn, Fe, and As in the lake porewater below the suboxic/anoxic boundary. The pond does not exhibit an oxic sediment-water interface, so as the primary minerals are deposited they do not undergo oxidation and subsequent dissolution and precipitation as oxyhydroxides. However, the amount of Mn and Fe in the pond-porewater indicates a significant source of oxyhydroxides, not associated with As. This project underscores the impact redox conditions have in controlling release and sequestration of metal(loids) in contaminated sediments. We suggest that the strategic development of wetlands in contaminated areas along the CDA River may be a viable part of a management strategy for decreasing metal(loid) bioavailability.